

RADIATION-MODIFIED POLY(TETRAFLUOROETHYLENE) RESIN FEEDS
AND A PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION

This invention relates to an improvement of thermal
5 properties of poly(tetrafluoroethylene) resin feeds by
ionizing radiations. More particularly, the invention
relates to a process for producing radiation-modified
poly(tetrafluoroethylene) resin feeds by applying ionizing
radiations to unsintered poly(tetrafluoroethylene) resins
10 under mild conditions so that only their melting
temperature is shifted to the lower end without changing
the quantities of heat of fusion and crystallization. The
thus modified poly(tetrafluoroethylene) resin feeds are
characterized in that their moldings have the same melting
15 temperature, heat of fusion, crystallization temperature
and heat of crystallization as the moldings of the
unirradiated poly(tetrafluoroethylene) resin feeds. The
invention also relates to the radiation-modified
poly(tetrafluoroethylene) resin feeds produced by the
20 process.

Poly(tetrafluoroethylene) resins are engineering
plastics having high resistance to heat, chemicals and
friction, high water repellency, good lubricating property
and high electrical insulation. Because of these features,
25 poly(tetrafluoroethylene) resins have heretofore been used
in various industrial and consumer applications including
electric wire coatings, tubes, pipes, packings, gaskets,
linings, insulation tape, bearings and roofing membranes

for air domes.

However, unlike the other polymeric materials, poly(tetrafluoroethylene) resins are seldom molded into various shapes on their own. For the very reason that they have high heat and chemical resistance, poly(tetrafluoroethylene) resins are difficult to shape by heating or dissolving in solvents.

With a view to improving the moldability of poly(tetrafluoroethylene) resins, it has been attempted to modify them by partial replacement of the tetrafluoroethylene molecules with a copolymerizable component. However, the introduced copolymerizable component not only causes substantial changes in thermal properties, such as the quantities of heat of fusion and crystallization, of the poly(tetrafluoroethylene) resins but also impairs their purity, thus causing deterioration in various characteristics of their moldings.

Of the various polymeric materials known today, poly(tetrafluoroethylene) resins are the easiest to deteriorate upon radiation exposure and the mechanical characteristics of their moldings decrease with absorbed dose whereas the quantities of heat of fusion and crystallization increase as more molecular chains are severed. Needless to say, poly(tetrafluoroethylene) resins in bulk powder form have substantially the same sensitivity to radiation as when they are shaped into moldings; following the exposure to radiation, the quantities of heat of fusion and crystallization increase as more molecular

chains are severed and the mechanical characteristics of shapes molded from the irradiated poly(tetrafluoroethylene) resins are also inferior to those of the unirradiated resins. These effects of radiations are currently used to
5 prepare a wax of poly(tetrafluoroethylene) resins by decomposing them.

It has recently been shown that poly(tetrafluoroethylene) resins are crosslinked by applying ionizing radiation in a special environment, i.e.
10 at elevated temperature in the absence of oxygen. The crosslinked resins have higher heat resistance but, on the other hand, their moldability is impaired.

SUMMARY OF THE INVENTION

It is, therefore, the principal object of the
15 invention to improve the moldability of poly(tetrafluoroethylene) resins by the simple means of applying radiation such that their purity is retained and that only their melting temperature is shifted toward the lower end without changing the quantities of heat of fusion
20 and crystallization from those of unsintered poly(tetrafluoroethylene) resins.

More specifically, the invention provides radiation-modified poly(tetrafluoroethylene) resins which are characterized in that their moldings have the same melting
25 temperature, heat of fusion, crystallization temperature and heat of crystallization as the moldings of the unirradiated poly(tetrafluoroethylene) resin feeds. The invention also provides a process for producing such

radiation-modified poly(tetrafluoroethylene) resin.

In order to attain the stated object, the present inventors applied ionizing radiations to unsintered poly(tetrafluoroethylene) resins in bulk powder form under various conditions and made a close study of the relationship between the exposure conditions and each of the thermal properties, such as melting temperature, heat of fusion, crystallization temperature and heat of crystallization, of the resins both before and after shaping. As a result of their intensive studies, the inventors found the following new fact: when unsintered poly(tetrafluoroethylene) resin feeds were exposed to ionizing radiation in an absorbed dose of no more than 1,000 Gy at room temperature in air, only their melting temperature was shifted toward the lower end without changing the quantities of their heat of fusion and crystallization, whereby their moldability was improved; in addition, the moldings of the irradiated resin feeds had identical values of thermal properties, such as melting temperature, heat of fusion, crystallization temperature and heat of crystallization, to those of the moldings prepared from the unirradiated resin feeds. The present invention has been accomplished on the basis of this finding.

The present inventors previously invented a method in which poly(tetrafluoroethylene) resins were exposed to ionizing radiation, thereby producing radiation-modified poly(tetrafluoroethylene) resins having increased tear

strength and an application for obtaining patent on this invention was already filed (Japanese Patent Application No. 2000-155902). The present invention provides a very effective method of using radiations in that the moldability of poly(tetrafluoroethylene) resin feeds could be improved by only shifting the melting temperature of unsintered resin feeds toward the lower end without affecting the thermal properties of the moldings to be prepared.

10 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the result of DSC (differential scanning calorimetry) conducted to measure thermal properties of 500-Gy irradiated poly(tetrafluoroethylene) in bulk power form in a temperature range of 270 - 390°C with the temperature rising at a rate of 10°C/min; and

Fig. 2 is a graph showing the result of DSC conducted to measure thermal properties of a comparative sample [unirradiated poly(tetrafluoroethylene) resin feed in bulk powder form] in a temperature range of 270 - 390°C with the temperature rising at a rate of 10°C/min.

DETAILED DESCRIPTION OF THE INVENTION

In the invention, a poly(tetrafluoroethylene) resin feed is treated by an ionizing radiation. To be more specific, a dried powder of poly(tetrafluoroethylene) resin or a liquid called "dispersion" in which a powder of poly(tetrafluoroethylene) resin is dispersed uniformly is treated by an ionizing radiation to give an absorbed dose

of 1 - 1,000 Gy in a temperature range of -30 ~ 50°C near ordinary or room temperature, preferably not higher than 19°C, and in air.

The term "poly(tetrafluoroethylene) resin feed" as
5 used herein means dried powders of
poly(tetrafluoroethylene) resins obtained by emulsion
polymerization or suspension polymerization, said powders
being optionally granulated or dispersed uniformly in
solvents or wetted with solvents. The powders or
10 dispersions of poly(tetrafluoroethylene) resins need not be
entirely treated with ionizing radiation and the intended
advantages and object of the invention can be attained even
if said powders or dispersions are mixed in suitable
proportions with the powders or dispersions of unirradiated
15 poly(tetrafluoroethylene) resins.

The dispersion medium, or the liquid in which the
powders of poly(tetrafluoroethylene) resin feeds can be
dispersed efficiently, may be exemplified by mixed
solvents such as those consisting of water/emulsifier,
20 water/alcohol, water/acetone, and water/alcohol/acetone;
suitable dispersion media can be easily selected or
prepared by skilled engineers in the art who are familiar
with dispersion media.

The emulsifier may be exemplified by an aqueous
25 colloidal suspension of PTFE which has a nonionic
surfactant such as NISSAN NONION HS208 (trademark) or an
anionic surfactant added in a few percent to the resin, or
a dispersion having an aqueous solution of phosphoric acid

or chromic acid added to the aqueous colloidal suspension of PTFE in order to provide ease in a subsequent step of bonding the resin film to a metal substrate by stoving.

The ionizing radiation to be used in the invention
5 may be exemplified by electron beams, x-rays, γ -rays, neutron beams and high-energy ions which may be used either alone or in admixture. The dose rate, or the amount of radiation applied per unit time, may be of any suitable values that can be easily chosen by skilled engineers in
10 the art.

The purpose of the invention can be easily attained by treating the poly(tetrafluoroethylene) resin feed with ionizing radiation in air. If desired, a certain kind of reactive gas or inert gas may intentionally be added to air
15 to create a special atmosphere so that a specified function or property is conferred to the radiation-modified poly(tetrafluoroethylene) resin or that a property such as water repellency the poly(tetrafluoroethylene) initially possess is attenuated; this practice is also included in
20 the scope of the invention. Therefore, the term "air" as defined herein covers not only the ordinary air in the atmosphere but also atmospheres created intentionally as described above by adjusting or modifying the composition of the ordinary atmospheric air.

25 The following examples are provided for the purpose of further illustrating the present invention but are in no way to be taken as limiting.

Example 1

A commercial fine powder of poly(tetrafluoroethylene) resin prepared by emulsion polymerization (CD 090 of Asahi Glass Fluoropolymers Co., Ltd.) was used as a resin feed and put into paper envelopes. The respective samples were
5 irradiated with γ -rays for 0.5, 2.5 and 5 hours at a dose rate of 200 Gy/h in air at room temperature, thus producing feed powders treated with γ -rays to absorbed doses of 100, 500 and 1,000 Gy.

Differential scanning calorimetry (DSC) provides a
10 simple tool for examining thermal properties of the poly(tetrafluoroethylene) resin both before sintering (in an unirradiated state) and after molding (in an irradiated state). The first run of scan with temperature elevation simulates thermal properties after polymerization reaction
15 whereas the second run of scan with temperature elevation simulates thermal properties after molding.

Thermal properties of the feed powder irradiated with 500 Gy of γ -rays were measured by DSC in a temperature range of 270 - 390°C with the temperature rising at a rate
20 of 10°C/min and the result is shown in Fig. 1. For comparison, the same measurement was made on an unirradiated poly(tetrafluoroethylene) resin powder and the result is shown in Fig. 2. The feed powders treated with γ -rays to absorbed doses of 100, 500 and 1,000 Gy were
25 subjected to the first and second runs of DSC and the melting temperature and the quantity of heat of fusion were measured for each sample; the results are shown in Table 1.

In the first run of DSC, the irradiated feed powders

exhibited lower melting temperatures than the unirradiated sample but there was little change in the quantity of heat of fusion. In the second run of DSC, there were no changes in thermal properties and all samples including the
5 comparative sample had the same data.

The term "heat flow rate" on the vertical axes of Figs. 1 and 2 represents a heat balance in thermal analysis by DSC, or the heat input to or output from the resin sample as it is heated or cooled with the temperature
10 rising or falling at a constant rate. The term "resin before sintering" refers to the case of using an unsintered shape as green PTFE and the term "resin after sintering" refers to the case of using a shape as a plastic after it is sintered, i.e. heat treated at the melting point or
15 above.

Table 1. Results of Analysis by DSC of Feed Powders for
Different Doses of Gamma-Rays

	First run		Second run	
	Melting temperature	Heat of fusion	Melting temperature	Heat of fusion
Unirradiated	338.1	68.5	325.1	30.1
100 Gy	337.7	68.1	325.3	30.8
500 Gy	337.0	66.7	325.1	30.2
1000 Gy	336.4	67.5	325.8	30.1

Example 2

20 A commercial molding powder of
poly(tetrafluoroethylene) resin prepared by suspension

polymerization (G 163 of Asahi Glass Fluoropolymers Co., Ltd.) was used as a resin feed and put into paper envelopes. The respective samples were irradiated with γ -rays for 1, 3 and 5 hours at a dose rate of 100 Gy/h in air at room temperature, thus producing feed powders treated with γ -rays to absorbed doses of 100, 300 and 500 Gy.

The feed powders treated with γ -rays to absorbed doses of 100, 300 and 500 Gy were subjected to the first and second runs of DSC in a temperature range of 270 - 390°C with the temperature rising at a rate of 10°C/min and the melting temperature and the quantity of heat of fusion were measured for each sample; the results are shown in Table 2.

In the first run of DSC, the irradiated feed powders exhibited lower melting temperatures than the unirradiated sample but there was little change in the quantity of heat of fusion. In the second run of DSC, there were no changes in thermal properties and all samples including the comparative sample had the same data.

Table 2. Results of Analysis by DSC of Feed Powders for Different Doses of Gamma-Rays

	First run		Second run	
	Melting temperature	Heat of fusion	Melting temperature	Heat of fusion
Unirradiated	342.6	63.7	325.6	21.3
100 Gy	338.4	62.4	325.9	21.7
300 Gy	337.0	63.2	326.1	22.2
500 Gy	335.9	62.0	325.8	22.1

Example 3

A commercial molding powder of poly(tetrafluoroethylene) resin prepared by suspension polymerization (G 350 of Asahi Glass Fluoropolymers Co., Ltd.) was used as a resin feed and put into paper envelopes. The respective samples were irradiated with γ -rays for 12, 30 and 60 minutes at a dose rate of 1,000 Gy/h in air at room temperature, thus producing feed powders treated with γ -rays to absorbed doses of 200, 500 and 1,000 Gy.

The feed powders treated with γ -rays to absorbed doses of 200, 500 and 1,000 Gy were subjected to the first and second runs of DSC in a temperature range of 270 - 390°C with the temperature rising at a rate of 10°C/min and the melting temperature and the quantity of heat of fusion were measured for each sample; the results are shown in Table 3.

In the first run of DSC, the irradiated feed powders exhibited lower melting temperatures than the unirradiated sample but there was little change in the quantity of heat of fusion. In the second run of DSC, there were no changes in thermal properties and all samples including the comparative sample had the same data.

Table 3. Results of Analysis by DSC of Feed Powders for
Different Doses of Gamma-Rays

	First run		Second run	
	Melting temperature	Heat of fusion	Melting temperature	Heat of fusion
Unirradiated	342.7	63.4	325.8	22.1
200 Gy	339.6	60.8	325.8	21.9
500 Gy	338.0	62.7	325.8	22.4
1000 Gy	337.3	62.3	325.4	23.1

Example 4

- 5 The powder irradiated with 1000 Gy of γ -rays in Example 3 was mixed uniformly at a ratio of 1:1 with an unirradiated powder of G 350 at a temperature of 15°C to prepare a feed powder. Thermal properties of the feed powder were measured by DSC in a temperature range of 270 -
- 10 390°C with the temperature rising at a rate of 10°C/min were. The feed powder was subjected to the first and second runs of DSC and the melting temperature and the quantity of heat of fusion were measured; the results are shown in Table 4.

15 Table 4. Results of Analysis by DSC of Feed Powders

	First run		Second run	
	Melting temperature	Heat of fusion	Melting temperature	Heat of fusion
Unirradiated	342.7	63.4	325.8	22.2
1:1 Mixture	338.2	63.8	325.6	22.5

If poly(tetrafluoroethylene) resin feeds after polymerization reaction but before sintering are treated with ionizing radiation by the method of the invention, only their melting temperature is shifted toward the lower
5 end without changing the quantities of their heat of fusion and crystallization. As a result, the moldability of the feeds is so much improved that the moldings prepared from them are the same as those from the unirradiated resin feeds not only in the melting temperature and the quantity
10 of heat of fusion but also in the crystallization temperature and the quantity of heat of crystallization. In addition, the improved moldability of the poly(tetrafluoroethylene) resins is anticipated to bring out new properties. What is more, the invention does not
15 rely upon chemical means of modification such as copolymerization and the inherent good properties of the poly(tetrafluoroethylene) resins remain intact; this will help further expand the scope of their utility.